



Europäisches Patentamt

European Patent Office

Office européen des brevets



⑪ Publication number:

0 600 421 A1

⑫

## EUROPEAN PATENT APPLICATION

㉑ Application number: 93119225.6

㉓ Int. Cl.5: C22C 38/00, C22C 33/02

㉒ Date of filing: 29.11.93

㉔ Priority: 30.11.92 JP 343145/92

㉕ Date of publication of application:  
08.06.94 Bulletin 94/23

㉖ Designated Contracting States:  
DE FR GB SE

㉗ Applicant: SUMITOMO ELECTRIC INDUSTRIES,  
LIMITED  
5-33, Kitahama 4-chome  
Chuo-ku  
Osaka 541(JP)

㉘ Inventor: Itoh, Yoshiaki, c/o Itami Works of  
Sumitomo  
Electric Industries, Ltd.,  
1-1, Koyakita 1-chome  
Itami-shi, Hyogo(JP)  
Inventor: Ito, Kozo, c/o Itami Works of  
Sumitomo  
Electric Industries, Ltd.,  
1-1, Koyakita 1-chome  
Itami-shi, Hyogo(JP)  
Inventor: Takeda, Yoshinobu, c/o Itami Works  
of Sumitomo  
Electric Industries, Ltd.,  
1-1, Koyakita 1-chome  
Itami-shi, Hyogo(JP)

㉙ Representative: Herrmann-Trentepohl,  
Werner, Dipl.-Ing.  
Patentanwälte Herrmann-Trentepohl,  
Kirschner, Grosse, Bockhorni & Partner  
Forstenrieder Allee 59  
D-81476 München (DE)

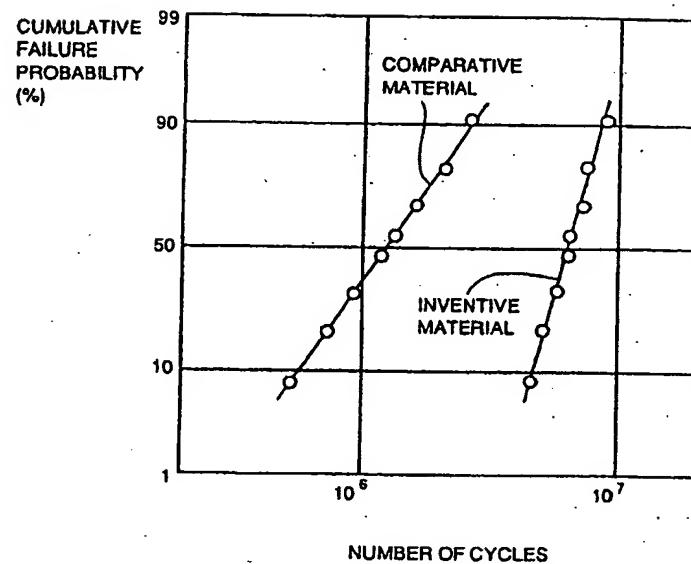
㉚ Low alloy sintered steel and method of preparing the same.

EP 0 600 421 A1

㉛ A low alloy sintered steel contains at least 0.15 percent by weight and less than 0.8 percent by weight of carbon. Its matrix is formed by a tempered martensite containing prior austenite crystal grains of not more than 15 µm in mean grain size. Pores and nonmetallic inclusions contained in the matrix are not more than 50 µm in maximum diameter, and density of the low alloy sintered steel is at least 96 percent of theoretical density. Raw material powder for the low alloy sintered steel includes iron alloy powder which is prepared by an atomizing process, and is treated with a dry mill in an inert gas atmosphere or in the atmospheric air. Thus, dislocations are introduced into the raw material powder, and nonmetallic inclusions contained in the raw material powder are pulverized to be not more than 50 µm in maximum diameter. Not only static characteristics but dynamic characteristics such as fatigue strength of the low alloy sintered steel are improved.

EP 0 600 421 A1

FIG. 2



## BACKGROUND OF THE INVENTION

### Field of the Invention

5 The present invention relates to a low alloy sintered steel for application to a machine structural part such as a gear or a race of a bearing which must have high fatigue strength, and a method of preparing the same.

### Description of the Background Art

10 Sintered machine parts of low alloy sintered steels which are prepared by powder metallurgy are widely applied to an automobile part, business equipment, a domestic electric product, an agricultural instrument and the like due to superior economic properties, and a demand for such sintered machine parts is increased year by year. With such increase of the demand, the low alloy sintered steels are increasingly required to have strict characteristics.

15 Various studies have been made to satisfy such requirements. As to compositions of the low alloy sintered steels, Fe-Ni-Mo-C, Fe-Ni-Cu-Mo-C and Fe-Cr-Mn-Mo-C low alloy sintered steels, for example, have been developed in addition to conventional Fe-Ni-C and Fe-Cu-C steels. As to raw material powder for the low alloy sintered steels, on the other hand, atomized powder which can facilitate improvement in density of sintered bodies is now taking place of reduced powder as generally employed.

20 Strength of a low alloy sintered steel has been remarkably improved by such technical developments. Static characteristics of the low alloy sintered steel, which are represented by tensile strength, are now approaching those of a general steel for machine structural use which is prepared by forging of I/M (Ingot Metallurgy) material. However, the low alloy sintered steel is yet insufficient in dynamic characteristics 25 represented by toughness and fatigue strength. In order to satisfy the requirement for characteristic improvement and further widen the range of application of the low alloy sintered steel, therefore, it is indispensable to improve the dynamic characteristics.

25 The most effective method for improving dynamic characteristics of a low alloy sintered steel which is prepared by powder metallurgy is to increase its density and reduce pores left in its interior. Powder forging is a generally known method of increasing density of a sintered steel. However, the dynamic characteristics 30 of a low alloy steel which is prepared by powder forging cannot exceed those of a general steel for machine structural use which is prepared in the same composition by forging of I/M material. Causes for such a disadvantage are an oxide film, which is formed on the surface of steel powder, hindering progress of sintering and causing segregation of alloying elements, difference between contents of nonmetallic inclusions 35 resulting from difference in steel producing technique between I/M and P/M (Powder Metallurgy) method, and pores left on a surface layer of a forged body. Japanese Patent Publication No. 57-8841 (1982) describes a method of separating/removing an oxide film which is formed on the surface of steel powder by mechanical pulverization. According to this method, however, it is impossible to remove nonmetallic inclusions which are also present in steel powder particles, although the oxide film provided on the surface 40 of the powder can be removed.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a low alloy sintered steel which has remarkably 45 improved dynamic characteristics such as fatigue strength in addition to excellent static characteristics, and a method of preparing the same.

A low alloy sintered steel according to an aspect of the present invention contains at least 0.15 percent by weight and less than 0.8 percent by weight of carbon. The matrix of this low alloy sintered steel is formed by a tempered martensite containing prior austenite crystal grains of not more than 15  $\mu\text{m}$  in mean 50 grain size. Pores and nonmetallic inclusions contained in the matrix are not more than 50  $\mu\text{m}$  in maximum diameter. Density of the low alloy sintered steel is at least 96 percent of theoretical density.

In a method of preparing a low alloy sintered steel according to another aspect of the present invention, raw powder containing at least either one of iron powder and iron alloy powder prepared by an atomizing process is treated in an inert gas atmosphere or in the atmospheric air by a dry mill so that dislocations are 55 introduced into the raw material powder and nonmetallic inclusions contained in the raw material powder are pulverized to not more than 50  $\mu\text{m}$  in maximum diameter. The as-treated raw material powder is softened/annealed. Carbon powder is so added and mixed to the softened/annealed raw material powder that the carbon content is at least 0.15 percent by weight and less than 0.8 percent by weight in the final

composition. The mixed powder is cold-formed into a compact. This compact is densified by sintering or hot plastic working to have density of at least 96 percent of theoretical density. The as-densified compact is heat-treated to provide a low alloy sintered steel having a matrix of a tempered martensite.

The term "low alloy sintered steel" herein employed indicates a generally known carbon steel of iron and carbon or a generally known low alloy steel of iron, carbon and other alloying elements, which is obtained by sintering raw material powder. On the other hand, the term "prior austenite crystal grains" indicates crystal grains, contained in the low alloy sintered steel, which have been austenite crystal grains in an austenite phase before quenching. In general, crystal grain sizes of quench hardened steels are compared as to those of such prior austenite crystal grains after martensitic transformation.

10 Fatigue strength of a steel, which is generally improved with increase in hardness, reaches a substantially constant level or is reduced when the hardness reaches a certain level, due to presence of nonmetallic inclusions. Improvement of the fatigue strength is conceivably stopped since small inclusions, which cannot form starting points at a low hardness level, define starting points of fatigue cracks as the hardness is improved. Therefore, it is expected possible to remarkably improve fatigue strength of a material which contains no inclusions, while it is difficult to industrially obtain such a material.

15 It is known that a fatigue life depends on a crack propagation rate at a high hardness level where improvement of fatigue strength is stopped. However, the crack propagation rate is remarkably reduced in the vicinity of grain boundaries. Therefore, it may be possible to attain improvement of fatigue strength when a structure containing a number of grain boundaries is achieved. In such a point of view, the present invention is adapted to improve dynamic characteristics of the low alloy sintered steel such as fatigue strength, by reducing pores for improving density of the steel while increasing grain boundaries by preparing the matrix from a particularly fine tempered martensite and minimizing sizes of the pores and nonmetallic inclusions.

20 According to the present invention, the matrix of the low alloy sintered steel is formed by a fine martensite containing prior austenite crystal grains of not more than 15  $\mu\text{m}$  in mean grain size. In order to obtain such a particularly fine martensite, it is necessary to refine the austenite before quenching. An exemplary method therefor is thermo-mechanical treatment such as ausforming in a general low alloy steel which is prepared by forging of VIM material. In the present invention employing powder metallurgy, on the other hand, it has been proved by the inventors that the most effective means is to treat raw material 25 powder in an inert gas atmosphere or in the atmospheric air with a dry mill such as a ball mill, a vibration mill or an attritor for a long time, for previously introducing a large amount of dislocations into the raw material powder. Namely, a large amount of dislocations are thus introduced into the raw material powder to refine the austenite before quenching, thereby obtaining a fine tempered martensite.

30 Further, it is possible to pulverize and refine nonmetallic inclusions contained in the raw material powder by the aforementioned treatment with the dry mill, thereby reducing large inclusions which are harmful for the fatigue strength. In other words, it has been proved possible to remarkably reduce influence exerted by the nonmetallic inclusions on fatigue strength of the low alloy sintered steel by reducing the maximum diameter thereof below 50  $\mu\text{m}$ , preferably below 25  $\mu\text{m}$ .

35 Hardness of powder which is treated with a dry mill is increased due to introduction of a large amount of dislocations. Therefore, it is difficult to cold-form the powder treated as such. Therefore, it is necessary to soften the treated powder by annealing, thereby improving compressibility. The annealing step is preferably carried out in a vacuum or in a non-oxidizing atmosphere at a temperature of at least 600 °C and not more than 1000 °C. If the annealing temperature is less than 600 °C, compressibility cannot be improved since the strain is insufficiently removed and the powder is softened merely at a small degree. When the annealing temperature exceeds 1000 °C, on the other hand, sintering so progresses between particles of the powder that the powder cannot be cold-formed unless pulverization is again carried out.

40 Carbon powder is mixed into the as-obtained treated powder, to adjust the content of carbon. Carbon is an important alloying element which controls the characteristics of the steel. As the carbon content is increased, the steel is increased in strength and hardness, and reduced in ductility. If the carbon content is less than 0.15 percent by weight, it is impossible to obtain excellent hardness after heat treatment. If the carbon content exceeds 0.8 percent by weight, on the other hand, an effect of improvement of hardness is at a small degree and fatigue strength is rather reduced by increase of retained austenite. Therefore, the carbon content of the low alloy sintered steel according to the present invention is set in a range of at least 0.15 percent by weight and less than 0.8 percent by weight.

45 The mixed powder obtained by adding and mixing carbon powder to the treated powder is cold-formed by a uniaxial press or through cold isostatic pressing (CIP), and thereafter densified to at least 96 percent of theoretical density by hot plastic working such as sintering or hot forging, hot extrusion, hot isotropic isostatic pressing (HIP) or the like at a temperature exceeding an  $A_3$  transformation point. After sintering,

working such as repressing, hot forging, hot extrusion or HIP is preferably performed in order to dissipate residual pores. The pores, which exert large influence on fatigue strength, can be regarded as equivalent to inclusions. Therefore, the maximum diameter of such pores must also be not more than 50  $\mu\text{m}$ , preferably not more than 25  $\mu\text{m}$ , similarly to the nonmetallic inclusions. The amount of residual pores is preferably not 6 more than 4 percent by volume.

When the treated powder containing a large amount of dislocations introduced by a dry mill is exposed to a high temperature in a densifying step of sintering or hot plastic working, the crystal grains are easily increased in diameter. In an effective method of preventing this, fine particles are homogeneously dispersed to pin migration of the grain boundaries. Such dispersed particles are effectively prepared from an oxide, a 10 nitride or a carbide which is not solidly solved in the matrix in a high-temperature austenite phase or has low solid solubility, such as alumina or aluminum nitride, for example. The mean grain size of such dispersed particles is not more than 0.5  $\mu\text{m}$ , preferably not more than 0.1  $\mu\text{m}$ . If the mean grain size of the dispersed particles exceeds 0.5  $\mu\text{m}$ , the dispersed particles themselves serve as sources of fatigue cracks. Further, ductility is reduced if the amount of the dispersed particles is increased. Therefore, the dispersed 15 particles are properly added in an amount of at least 0.5 percent by volume and not more than 5 percent by volume with respect to the treated powder.

The as-obtained sintered body or hot plastic worked body is reinforced by ordinary heat treatment through transformation from an austenite to a martensite, thereby forming the inventive fine tempered low alloy sintered steel. In more concrete terms, the sintered body or the hot plastic worked body is heated to 20 and held at the austenite phase, oil-quenched and thereafter tempered. It is also effective to perform carburization, carbonitriding, nitriding, surface hardening by induction heating or the like in combination with the heat treatment.

The low alloy sintered steel according to the present invention may be in the composition of a well-known carbon steel or low alloy steel, as hereinabove described. However, the present invention employing 25 powder metallurgy has a preferable alloy composition due to its process restriction. Examples of such a preferable alloy composition are Fe-Ni-Mo-C and Fe-Cr-Mo-Mn-C. An Fe-Cr-Mo-Mn-C low alloy sintered steel is superior in Hardenability to an Fe-Ni-Mo-C low alloy sintered steel, while the same is sensitive to a heating atmosphere for sintering or forging, due to the metal elements such as Cr and Mn which are easy to oxidize. Therefore, selection and control of an atmosphere for powder treatment and heating are 30 important.

In the aforementioned alloy composition, Ni remarkably improves Hardenability, while this effect cannot be attained if the Ni content is less than 0.5 percent by weight. When the Ni content exceeds 3 percent by weight, on the other hand, it is difficult to cold-form the powder and retained austenite is increased after heat treatment, to exert harmful influence on fatigue strength. On the other hand, a small amount of Mo 35 improves Hardenability, and forms a carbide with carbon to improve wear resistance and heat resistance. However, these effects cannot be attained if the Mo content is less than 0.1 percent by weight, while compressibility is deteriorated by solid-solution hardening if the Mo content exceeds 1.5 percent by weight. Further, Cr has functions of remarkably improving Hardenability and increasing temper softening resistance. However, the effect of improving Hardenability cannot be attained if the Cr content is less than 0.5 percent 40 by weight, while compressibility is reduced by solid-solution hardening if the Cr content exceeds 3 percent by weight. In addition, Mn improves Hardenability and acts as a deoxidizer and a desulfurizer in preparation of powder, to reduce the oxygen content in the powder. However, the effect of improving Hardenability cannot be attained if the Mn content is less than 0.2 percent by weight, while compressibility is deteriorated by solid-solution hardening if the Mn content exceeds 1.6 percent by weight.

45 While grain growth at a high temperature can be effectively suppressed by pinning through dispersed particles as hereinabove described, it is also effective to add an element forming a carbide or a nitride having low solid solubility in an austenite phase to the raw material alloy powder. According to this method, it is possible to suppress growth of crystal grains in austenitizing, thereby further refining grain sizes of the prior austenite crystal grains. Such an element is preferably prepared from niobium, vanadium, titanium, 50 tungsten or aluminum, preferably in an amount of at least 0.05 percent by weight and not more than 3.0 percent by weight in total. The effect of suppressing growth of crystal grains cannot be attained if the amount is less than 0.05 percent by weight, while the crystal grains are no longer refined and compressibility of the powder is rather reduced by solid-solution hardening if the amount exceeds 3.0 percent by weight.

55 In the inventive low alloy sintered steel, the crystal grains are so extremely reduced that the grain boundaries are increased. Therefore, portions forming nuclei of transformation are increased to facilitate transformation from  $\gamma$  (austenite) to  $\alpha$  (ferrite) +  $\text{Fe}_3\text{C}$  (cementite), leading to deterioration of Hardenability. However, boron can reduce functions of the grain boundaries serving as nucleation sites by segregating in

the austenite grain boundaries and reducing energy thereof. Thus, it is possible to improve hardenability by adding a small amount of boron. In order to attain this effect, it is necessary to add at least 10 ppm of boron in weight fraction. If the amount of boron exceeds 300 ppm, however, improvement of hardenability can no longer be attained and the steel is embrittled due to reduction in strength of the grain boundaries.

According to the present invention, as hereinabove described, it is possible to provide a low alloy sintered steel which is excellent not only in static characteristics but in dynamic characteristics such as fatigue strength and toughness. Thus, the inventive low alloy sintered body is particularly useful as a machine structural part such as a gear or a clutch part which must have high fatigue strength, while it is expected that the same can be applied to a field in which no such low alloy sintered steel has been employed in general.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

#### 15 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing distribution of hardness (Rockwell C hardness) corresponding to distances from surface obtained by a Jominy test in relation to an inventive material containing boron, another inventive material containing no boron and an SCM420 steel material;

20 Fig. 2 is a graph showing cumulative failure probabilities indicating lives of outer races prepared by an inventive material and a comparative SCM420 steel material with respect to flaking etc. in a clutch stroking test; and

Fig. 3 is a graph showing wear resistance of the outer races and the sprags prepared by the inventive material and the comparative SCM420 steel material.

#### 25 DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### Example 1

30 Commercially available iron alloy powder materials prepared by a water atomizing process to have AISI4600 compositions (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo) were treated with a high energy dry mill in an argon atmosphere at various treatment times of 2, 3, 4, 20, 40 and 80 hours. Each of the treated powder materials was heated in a nitrogen atmosphere at a temperature of 800°C for 1 hour to be annealed/softened, and graphite powder was added and mixed to the treated powder so that the carbon content was 0.25 percent by weight in the final composition. Thereafter each treated powder was cold-formed by a die press so that green density was 6.9 g/cm<sup>3</sup> (density ratio of 0.878 to theoretical density). Each of the compacts was sintered in nitrogen at a temperature of 1150°C for 1 hour, and further forged at this temperature, to obtain a forged body having a density ratio of at least 0.99 to the theoretical density.

Each forged body was carburized at a temperature of 910°C so that an effective case depth was 1 mm, 40 then held at a temperature of 850°C, thereafter quenched in oil, and tempered at a temperature of 200°C for 90 minutes. The respective low alloy sintered steels thus obtained were subjected to measurement of mean grain sizes of prior austenite ( $\gamma$ ) crystal grains, maximum diameters of pores and inclusions in areas of 400 mm<sup>2</sup>, transverse rupture strength values and fatigue strength values. Table 1 shows the results of the measurement. The fatigue strength values were obtained by a rotary bending test using smoothed test pieces, while the transverse rupture strength values were obtained using smoothed test pieces of 4 mm x 9 mm x 45 mm in size.

## EP 0 600 421 A1

Table 1

Sample	Treatment Time (hr)	Prior $\gamma$ Grain Size ( $\mu\text{m}$ )	Maximum Diameter Inclusion ( $\mu\text{m}$ )	Transverse of Rupture Strength ( $\text{kg/mm}^2$ )	Fatigue Strength ( $\text{kg/mm}^2$ )
1	2	18.7	186	220	80
2	3	15.0	48	230	85
3	4	12.6	47	244	90
4	20	10.4	33	261	95
5	40	8.8	25	277	100
6	80	8.2	27	273	100

It is understood from the results of Table 1 that the mean grain sizes of prior austenite crystal grains and the sizes of the maximum inclusions were reduced as the times for treating raw material powder with the dry mill were increased and characteristics of the low alloy sintered steels were improved in response, to provide low alloy sintered steels having fatigue strength values of at least  $85 \text{ kg/mm}^2$  in particular.

Example 2

Commercially available iron alloy powder materials prepared by a water atomizing process to have AISI4600 compositions (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo) were treated with a high energy dry mill in an argon atmosphere for 40 hours. Each of the as-obtained treated powder materials was heated in a nitrogen atmosphere at a temperature of  $800^\circ\text{C}$  for 1 hour to be annealed/softened, and thereafter graphite powder was added and mixed to the treated powder so that the carbon content was 0.25 percent by weight in the final composition. This mixed powder was cold-formed by a die press so that green density was  $6.9 \text{ g/cm}^3$  (density ratio of 0.878). Thereafter the compacts were sintered in nitrogen at a temperature of  $1150^\circ\text{C}$  for 1 hour, and further forged at this temperature, so that density ratios after forging were varied in a range of 0.92 to 0.99.

The forged bodies having different density ratios were heat treated similarly to Example 1, and subjected to measurement of mean grain sizes of prior austenite ( $\gamma$ ) crystal grains, transverse rupture strength values, impact values and fatigue strength values. Table 2 shows the results of the measurement. The respective low alloy sintered steels contained pores and inclusions of not more than  $50 \mu\text{m}$  in maximum diameter. For the purpose of comparison, a low alloy sintered steel was prepared in a similar manner to the above except that raw material powder was not treated with a dry mill, and subjected to the same evaluation as the above. Table 2 also shows the results.

Table 2

Sample	Density Ratio	Prior $\gamma$ Grain Size ( $\mu\text{m}$ )	Transverse Rupture Strength ( $\text{kg/mm}^2$ )	Impact Value ( $\text{kgf}\cdot\text{m}/\text{cm}^2$ )	Fatigue Strength ( $\text{kg/mm}^2$ )
7	0.92	8.8	202	0.66	70
8	0.94	8.9	221	0.92	75
9	0.96	8.8	248	1.4	85
10	0.99	8.7	277	3.2	100
Comparative Material	0.99	22.4	210	1.72	75

It is understood from the results shown in Table 2 that all of strength, toughness (impact value) and fatigue strength values of the low alloy sintered steels were increased as the density ratios were increased. When the density ratios reached 0.96, low alloy sintered steels having fatigue strength values of at least  $85 \text{ kg/mm}^2$  were obtained. In the comparative material prepared with no step of treating the raw material powder with a dry mill, however, strength and fatigue strength values were inferior to those of the inventive low alloy sintered steels due to a large mean grain size of prior austenite crystal grains, even if a low alloy sintered steel having a high density ratio was prepared.

Example 3

Commercially available iron alloy powder materials prepared by a water atomizing process to have AISI4600 compositions (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo) were blended and mixed with alumina powder materials of 0.05  $\mu\text{m}$  in mean particle size so that volume fractions of the alumina powder materials were 0.5, 1.0, 2.0 and 5.0 percent respectively. Thereafter each of the mixed powder materials was treated with a high energy dry mill in an argon atmosphere for 40 hours. Each of the treated powder materials was annealed/softened, mixed with graphite powder, cold-formed, sintered, forged to have a density ratio of at least 0.99 and heat treated under the same conditions as Example 1, to prepare a low alloy sintered steel.

The respective low alloy sintered steels as obtained were subjected to measurement of mean grain sizes of prior austenite crystal grains, transverse rupture strength values, impact values and fatigue strength values. Table 3 shows the results of the measurement. Pores and inclusions contained in the respective low alloy sintered steels were not more than 50  $\mu\text{m}$  in maximum diameter.

16

Table 3

Sample	Al <sub>2</sub> O <sub>3</sub> Content (vol%)	Prior $\gamma$ Grain Size ( $\mu\text{m}$ )	Transverse Rupture Strength (kg/mm <sup>2</sup> )	Impact Value (kgf $\cdot$ m/cm <sup>2</sup> )	Fatigue Strength (kg/mm <sup>2</sup> )
11	0.5	7.8	279	3.4	100
12	1.0	4.8	330	6.1	120
13	2.0	2.9	338	6.7	120
14	5.0	2.5	342	5.9	120

25

It is understood from the results shown in Table 3 that prior austenite crystal grains were refined by addition of alumina. It is also understood that the effect of such refinement was stopped and the impact value (toughness) was reduced when the amount of alumina exceeded 5 percent by volume.

30

Example 4

Alumina powder materials having mean particle sizes of 0.05, 0.1, 0.5, 5, 15 and 24  $\mu\text{m}$  were blended and mixed to commercially available iron alloy powder materials prepared by a water atomizing process to have AISI4600 compositions (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo) so that volume fractions of the alumina powder materials were 1.0 percent. Thereafter each of the mixed powder materials was treated with a high energy dry mill in an argon atmosphere for 40 hours. Each of the as-obtained treated powder materials was annealed/softened, mixed with graphite powder, cold-formed, sintered, forged to have a density ratio of at least 0.99, and heat treated under the same conditions as Example 1, to prepare a low alloy sintered steel.

The respective low alloy sintered steels as obtained were subjected to measurement of mean grain sizes of prior austenite ( $\gamma$ ) crystal grains, transverse rupture strength values, impact values and fatigue strength values. Table 4 shows the results of the measurement.

Table 4

Sample	Al <sub>2</sub> O <sub>3</sub> Particle Size ( $\mu\text{m}$ )	Prior $\gamma$ Grain Size ( $\mu\text{m}$ )	Transverse Rupture Strength (kg/mm <sup>2</sup> )	Impact Value (kgf $\cdot$ m/cm <sup>2</sup> )	Fatigue Strength (kg/mm <sup>2</sup> )
15	0.05	4.8	330	6.1	120
16	0.1	6.2	315	4.4	120
17	0.5	10.8	272	3.2	115
18	5	14.2	232	2.0	80
19	15	17.3	218	1.8	78
20	24	22.2	212	1.6	75

55

It is understood from the results shown in Table 4 that prior austenite crystal grains contained in the low alloy sintered steels were refined and fatigue strength values exceeding 85 kg/mm<sup>2</sup> were attained by addition of alumina powder of not more than 0.5  $\mu\text{m}$  in mean particle size. It is also understood that the effect of such refinement of the prior austenite crystal grains could not be attained and alumina rather

functioned as a defect in a tendency of reducing strength and toughness when the mean particle sizes of the as-added alumina powder exceeded 5  $\mu\text{m}$ .

Example 5

5 Ferroniobium powder, titanium powder, ferrovanadium powder, tungsten powder and ferroaluminum powder for serving as niobium, titanium, vanadium, tungsten and aluminum sources were added and mixed to commercially available iron alloy powder materials prepared by a water atomizing process to have AISI4100 compositions (Fe - 0.8 wt.% Mn - 1.0 wt.% Cr - 0.25 wt.% Mo) so that the contents thereof were  
 10 0.5 percent by weight in final compositions, and the powder materials were treated with a high energy dry mill in an argon atmosphere for 40 hours.

Each of the treated powder materials was heated in a nitrogen atmosphere at a temperature of 800 °C for 1 hour, to be annealed/softened. Thereafter graphite powder was added/mixed to each treated powder material so that the carbon content was 0.2 percent by weight in the final composition. Each mixed powder  
 15 was cold-formed, sintered and forged similarly to Example 1, to obtain a forged body having a density ratio of at least 0.99 after forging. Each forged body was gas-carburized so that an effective case depth was 1 mm, thereafter heated at a temperature of 850 °C, quenched in oil, and thereafter tempered at a temperature of 200 °C for 90 minutes.

The respective low alloy sintered steels were subjected to measurement of mean grain sizes of prior  
 20 austenite ( $\gamma$ ) crystal grains, transverse rupture strength values, impact values and fatigue strength values. Table 5 shows the results of the measurement. The respective low alloy sintered steels contained pores and inclusions of not more than 50  $\mu\text{m}$  in maximum diameter.

Table 5

Sample	Added Element	Prior $\gamma$ Grain Size ( $\mu\text{m}$ )	Transverse Rupture Strength (kg/mm <sup>2</sup> )	Impact Value (kgf·m/cm <sup>2</sup> )	Fatigue Strength (kg/mm <sup>2</sup> )
21	None	8.8	277	3.2	100
22	Nb	6.2	321	4.9	120
23	Ti	7.7	318	4.9	115
24	V	6.5	310	4.8	120
25	W	7.2	316	5.1	120
26	Al	6.3	319	5.0	118

It is understood from the results shown in Table 5 that refinement of prior austenite crystal grains was facilitated by addition of niobium, titanium, vanadium, tungsten and aluminum, so that the low alloy sintered steels were further improved in strength and toughness (impact value) as compared with that containing no such element.

Example 6

1 percent by volume of alumina powder having a mean particle size of 0.05  $\mu\text{m}$  was mixed to a commercially available iron alloy powder material prepared by a water atomizing process to have an AISI4600 composition (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo). Thereafter each of the mixed powder materials was treated with a high energy dry mill in an argon atmosphere for 40 hours. Each of the treated powder was annealed/softened under the same conditions as Example 1, and then mixed with graphite powder and ferroboron powder so that the carbon content was 0.25 percent by weight and a boron content was 30 ppm in weight fraction in the final composition. This mixed powder material was cold-formed, sintered and forged, to obtain a forged body having a density ratio of at least 0.99.

A round bar of 25.4 mm in diameter by 101.6 mm in length (1 inch in diameter by 4 inches in length) was cut from the forged body, and subjected to a Jominy test for evaluation of hardenability. For the purpose of comparison, round bars of the same shapes as the above were cut from the forged body (sample No. 12), which was prepared in Example 3 to contain 1.0 percent by volume of alumina and no boron, and an SCM420 steel material, and also subjected to comparison/evaluation of hardenability. Fig. 1 shows the results. It is understood from Fig. 1 that hardenability of the inventive material (sample No. 12) containing no B (boron) was reduced by refinement of prior austenite crystal grains. It is also understood that hardenability of the inventive material containing B (boron) according to this Example was remarkably

improved to a substantially equivalent level to the SCM420 steel material.

#### Example 7

5      1 percent by volume of alumina powder having a mean particle size of  $0.05 \mu\text{m}$  was mixed to commercially available iron alloy powder prepared by a water atomizing process to have an AISI4600 composition (Fe - 1.8 wt.% Ni - 0.5 wt.% Mo). Thereafter the mixed powder was treated with a high energy dry mill in an argon atmosphere for 40 hours. The treated powder was annealed/softened in a vacuum at a temperature of  $1000^\circ\text{C}$  for 1 hour, and thereafter mixed with graphite powder so that the carbon content  
 10     was 0.25 percent by weight in the final composition. This mixed powder was cold-formed in a similar manner to Example 1, to prepare a compact having a part shape of a one-way clutch.

The compact was sintered, forged and heat-treated similarly to Example 1, and thereafter worked by polishing etc. into an outer race and a sprag of a one-way clutch for application to an automatic transmission for an automobile. For the purpose of comparison, the same outer race and sprag were  
 15     prepared from a similarly heat-treated SCM420 material. The outer races and the sprags of the inventive and comparative materials were employed to assemble clutches, which were then subjected to a stroking test. Test conditions were as follows:

#### Stroking Test Conditions

20     Load Torque: 600 N·m  
 Rocking Speed: 600 cpm  
 Oil Feed Temperature:  $120 \pm 5^\circ\text{C}$   
 Lubricating Method: Oil Bath  
 25     Lubricating Oil: AT Oil  
 Inner Race: Material: SUJ2  
 Heat Treatment: Quench-and-Temper  
 Hardness: HRC61 to 63

30     Fig. 2 shows cumulative failure probabilities caused by flaking etc. as to the outer races of the inventive and comparative materials, as the results of the aforementioned endurance test. It is understood from Fig. 2 that the inventive material is superior in life with respect to flaking etc. to the comparative material of the conventional SCM420 carburized steel material. In the aforementioned endurance test, further, wear rates of the outer races and the sprags were measured at  $10^4$ ,  $10^5$  and  $10^6$  cycles respectively. Fig. 3 shows the results. It is understood from Fig. 3 that the inventive material was superior in wear resistance to the  
 35     comparative material of the conventional SCM420 carburized steel material.

According to the present invention, as hereinabove described, it is possible to provide a low alloy sintered steel which is excellent not only in static characteristics such as transverse rupture strength but dynamic characteristics such as fatigue strength and an impact value (toughness).

Although the present invention has been described and illustrated in detail, it is clearly understood that  
 40     the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

#### Claims

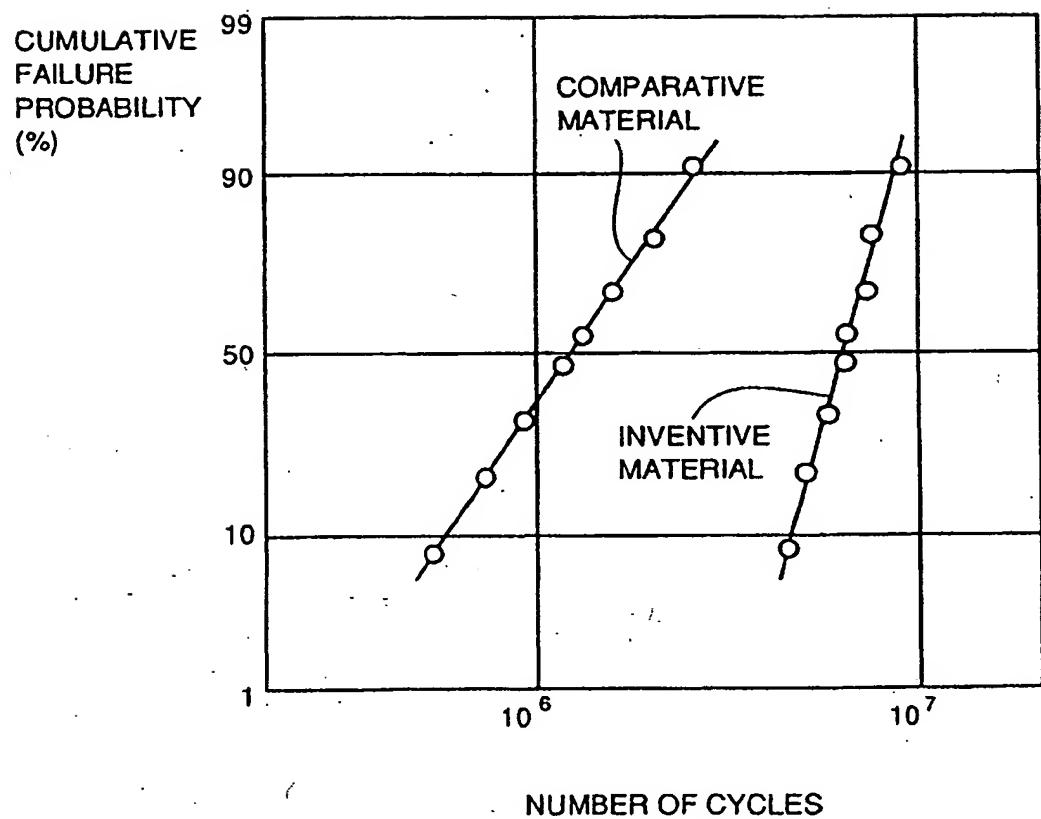
45     1. A low alloy sintered steel containing at least 0.15 percent by weight and less than 0.8 percent by weight of carbon, being provided with a matrix of a tempered martensite containing prior austenite crystal grains of not more than  $15 \mu\text{m}$  in mean grain size, said matrix containing pores and nonmetallic inclusions of not more than  $50 \mu\text{m}$  in maximum diameter, and having density of at least 96 percent of theoretical density.  
 50     2. The low alloy sintered steel in accordance with claim 1, wherein  
 particles of not more than  $0.5 \mu\text{m}$  in mean particle size, being not solidly solved in an austenite phase or having low solid solubility and being prepared from at least one selected from a group of oxide, nitride and carbide are homogeneously dispersed in said matrix.  
 55     3. The low alloy sintered steel in accordance with claim 1, wherein  
 : said low alloy sintered steel contains at least 10 ppm and not more than 300 ppm by weight of boron.

EP 0 600 421 A1

4. The low alloy sintered steel in accordance with claim 1, wherein  
said low alloy sintered steel contains at least one element selected from a group of niobium, vanadium, titanium, tungsten and aluminum in an amount of at least 0.05 percent by weight and not more than 3.0 percent by weight in total.
5. The low alloy sintered steel in accordance with claim 1, wherein  
said low alloy sintered steel contains at least 0.5 percent by weight and not more than 3 percent by weight of nickel and at least 0.1 percent by weight and not more than 1.5 percent by weight of molybdenum.
6. The low alloy sintered steel in accordance with claim 1, wherein  
said low alloy sintered steel contains at least 0.5 percent by weight and not more than 3 percent by weight of chromium, at least 0.1 percent by weight and not more than 1.5 percent by weight of molybdenum, and at least 0.2 percent by weight and not more than 1.6 percent by weight of manganese.
7. A method of preparing a low alloy sintered steel, comprising the steps of:  
treating raw material powder containing at least either one of atomized iron powder and atomized iron alloy powder in an inert gas atmosphere or in the atmospheric air with a dry mill, thereby introducing dislocations into said raw material powder and pulverizing nonmetallic inclusions being contained in said raw material powder to not more than 50  $\mu\text{m}$  in maximum diameter;  
softening/annealing said treated raw material powder;  
adding and mixing carbon powder to said softened/annealed raw material powder to attain a carbon content of at least 0.15 percent by weight and less than 0.8 percent by weight in the final composition;  
obtaining a compact by cold-forming said mixed powder;  
densifying said compact to have density of at least 96 percent of theoretical density by sintering or hot plastic working; and  
heat treating said densified compact thereby obtaining a low alloy sintered steel having a matrix of a tempered martensite.
8. The method of preparing a low alloy sintered steel in accordance with claim 7, wherein  
said step of treating said raw material powder with a dry mill includes a step of adding and mixing particles of not more than 0.5  $\mu\text{m}$  in mean particle size, being not solidly solved in an austenite phase or having low solid solubility and being prepared from at least one selected from a group of oxide, nitride and carbide, to said raw material powder and thereafter treating the as-obtained mixture with said dry mill.
9. The method of preparing a low alloy sintered steel in accordance with claim 8, wherein  
said particles are added to said raw material powder to be in a volume fraction of at least 0.5 percent by volume and not more than 5 percent by volume with respect to overall said treated powder.
10. The method of preparing a low alloy sintered steel in accordance with claim 8, wherein  
said added particles are alumina particles.
11. The method of preparing a low alloy sintered steel in accordance with claim 7, wherein  
said step of treating said raw material powder with a dry mill includes a step of adding and mixing at least one element selected from a group of niobium, vanadium, titanium, tungsten and aluminum to said raw material powder to be in a content of at least 0.05 percent and not more than 3 percent by weight in total and thereafter treating the as-obtained mixture with said dry mill.
12. The method of preparing a low alloy sintered steel in accordance with claim 7, wherein  
said step of softening/annealing said treated raw material powder is carried out in a vacuum or a non-oxidizing atmosphere at a temperature of at least 600 °C and not more than 1000 °C.
13. The method of preparing a low alloy sintered steel in accordance with claim 7, further comprising a step of adding and mixing ferroboron powder to said softened/annealed raw material powder to attain a boron weight fraction of at least 10 ppm and not more than 300 ppm.

EP 0 600 421 A1

FIG. 2



NUMBER OF CYCLES

EP 0 600 421 A1

FIG. 2

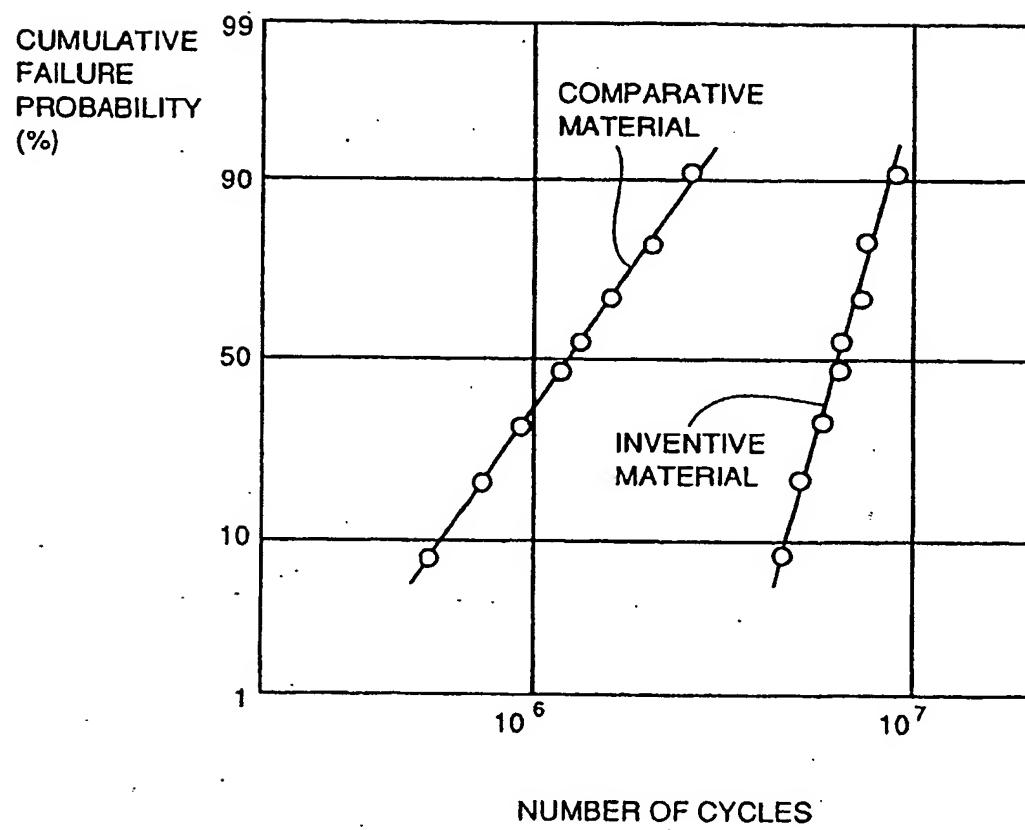
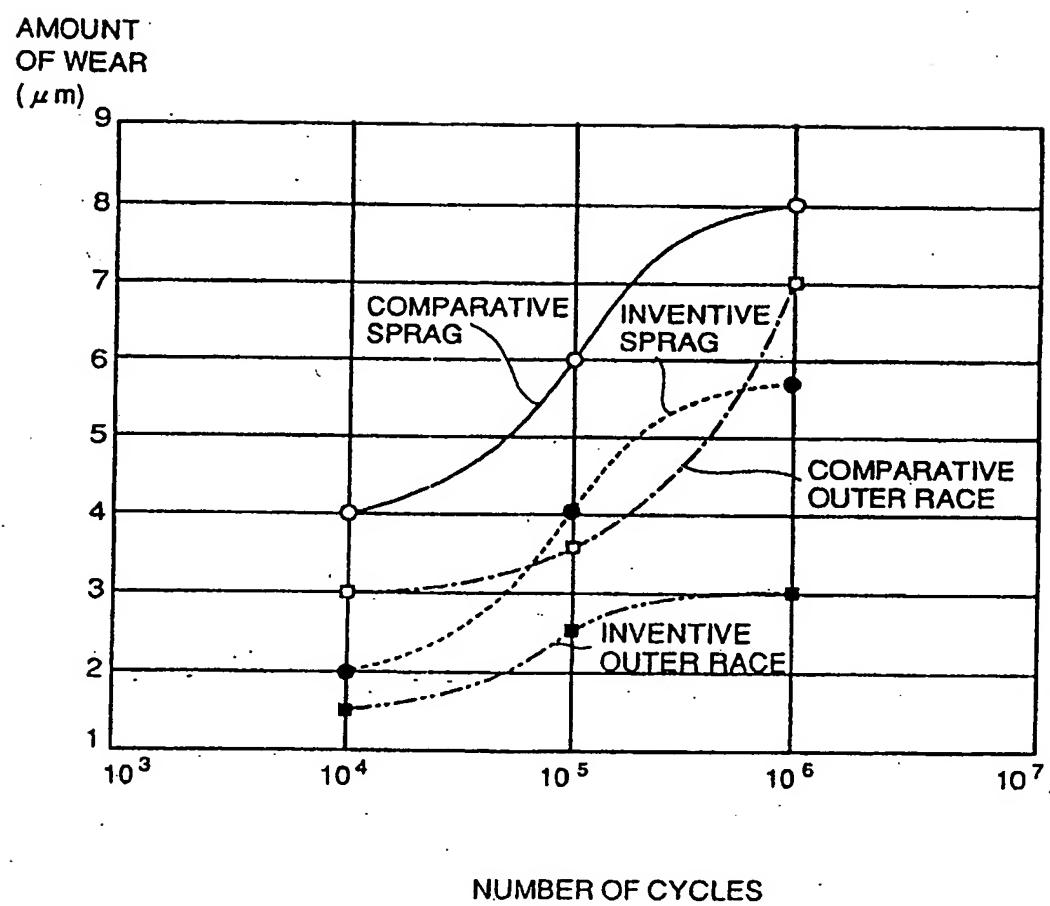


FIG. 3





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 9225

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CLS)
X	GB-A-2 219 004 (DORYOKURO KAKUNENRYO KAIHATSU JIGYODAN, KOBE STEEL LTD, SUMITOMO METAL) 29 November 1989 * CLAIM 1, PAGE 15, LINES 12-23, TABLE 1, EXAMPLE 12 *	1-4, 7-9, 11	C22C38/00 C22C33/02
Y	---	1-4, 6-9, 11	
Y	GB-A-2 065 700 (UDDEHOLMS AB) 1 July 1981 * ABSTRACT, CLAIMS 13, 14 *	1-4, 6-9, 11	
X	DE-A-25 55 679 (STORA KOPPARBERGS BERGLAGS AB) 1 July 1976 * PAGE 7, LINES 9-24, TABLE 1*	1-3	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
MUNICH	22 March 1994	Pivalica-Bjoerk, P	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published no, or after the filing date D : document cited to the application L : document cited for other reasons & : member of the same patent family, corresponding document	